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# **The Geological History of Water: From Earth's Accretion to the Modern Deep Water Cycle**

#### **Lars Rüpke1 and Fabrice Gaillard2**

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**The abundance of water on Earth and its distribution between surficial and deep reservoirs are the outcome of 4.6 billion years of geological history involving various mechanisms of water in and outgassing. Here, we use the metaphor of a pipeline connecting Earth's deep and surface water reservoirs. The net flux through this pipeline has changed over time due to contrasting Hadean, Archean, and modern geodynamic regimes. Most water was dissolved in the primordial magma ocean, entrapped in the solidifying mantle, and massively released by volcanism during the Hadean and Archaean. As Earth cooled, plate tectonics enabled water ingassing into the mantle, which appears to exceed outgassing under the modern tectonic regime, implying that Earth's surface has been drying out and will continue to do so.** 

**Keywords: hydrogen; water cycle; early Earth; subduction zones; geodynamics**

#### **INTRODUCTION**

The amount of free water on Earth's surface is controlled by the competition between  $H_2O$  outgassing by volcanism and H2O fixation within rock-forming minerals. Mantle convection enables hydrous minerals on Earth's surface to be recycled into the mantle by plate subduction, resulting in mantle ingassing and the concept of Earth's geological water cycle, which is unique in the Solar System. In this paper, we refer to a water pipeline that allows for  $H_2O$ transfer between Earth's interior mantle and exterior surface, sometimes called the exosphere. This pipeline is reactive because water can be stored and transported in various chemical forms and evolutive because the nature of mantle ingassing and outgassing evolves with the geological state of the planet, which has greatly changed from Earth's birth to present-day time.

All mineral phases in planetary interiors can dissolve H2O to concentration levels ranging from weight part per million (wt. ppm) to weight percent (wt.%). The water solubility, here defined as the maximum amount of water that silicates can store in equilibrium with an aqueous fluid phase, generally decreases in the order silicate melt > wadsleyite > ringwoodite > pyroxenes > olivine > mantle garnets. Water solubility in the bridgmanite phase of the lower mantle appears to be generally low, but there are still some contradictions in experimental data. Fe–Ni metals are also able to store significant amounts of hydrogen. Each H2O solubility law is affected by the intensive parameters, pressure, temperature, and oxygen fugacity. The spatial

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amounts remain debated (Tagawa et al. 2021; Broadley et al. 2022). Geochemical arguments suggest that the mantle has lost most of its initial water, containing only about 0.5 to 1.3 oceans today. However, its storage capacity may be much higher, especially in the transition zone at 410 to 660 km depth.

#### **THE GEOLOGICAL HISTORY OF WATER**

Figure 1 summarizes 4.6 Gy of the geological history of water. Earth's water and building blocks, hydrogen and oxygen, were present at the time of accretion, most likely sourced from chondritic materials and the possible capture of nebular gas (Broadley et al. 2022). As magma ocean conditions prevailed during the planetary and planetary embryo stages, most hydrogen was dissolved in the molten silicate proto-Earth as  $H_2$  and  $H_2O$ . At the same time, the surrounding atmosphere contained molecular  $H_2$  but almost no H2O (Gaillard et al. 2022). Gaseous species were lost to space due to low gravity in small bodies and impacts in larger bodies. During planetary embryo to planetary stages, significant amounts of hydrogen could also have dissolved in the forming metallic core (Tagawa et al. 2021), which, together with escape processes, limited the amount of H2O that the bulk silicate Earth (BSE) was able to accrete during these early stages.

If the solar nebula was still present when the planet reached the size of approximately half the present-day Earth, gravitational capture of  $H_2$  would become possible (Broadley et al. 2022). Changes in iron oxidation, induced by the high pressure at the base of the magma ocean, made the magma ocean's shallower parts and the atmosphere oxidized (Armstrong et al. 2019). These modifications enhanced the storage of  $H<sub>2</sub>O$  in the magma ocean and hydrogen in the core. Following the moon-forming impact and the associated loss of the early atmosphere, a late veneer of chondritic materials may have completed the volatile inventory of the bulk silicate Earth (Broadley et al. 2022),

High-temperature discharge at the Turtle Pits hydrothermal site on the Mid-Atlantic Ridge. Photo taken by ROV Kiel 6000 in a water depth of 2986 m.

water within Earth's interior and modulated the amount of surficial water throughout its history. This evolution formed four major interconnected reservoirs: ocean, continental crust, mantle, and core. The modern ocean contains approximately 1.4  $\times$  10<sup>21</sup> kg of water, continental crust about five times less, and the core is also thought to have played an important role in partitioning hydrogen in the early Earth, but the involved

and temporal evolution of these intensive parameters, and the style of prevailing geodynamics, have shaped the distribution of



but its importance for Earth's total water budget remains debated. The currently available data point to comets contributing only minor amounts to the total  $H_2O$  budget (Broadley et al. 2022), but a significant contribution to early surface waters remains a possibility.

The progressive solidification of the magma ocean involved a complex interplay of thermal, rheological, mechanical, and petrological processes to which no unique solution has so far been defined. Most scenarios point to a magma ocean that crystallized from the bottom up with water being trapped in the mantle upon solidification due to the persistence of partially molten regions (mushes) and the entrapment of melt-rich pockets at depth (Korenaga 2021; Bower et al. 2022). The onset of sub-solidus convection progressively moved mantle material into the melt extraction window, enabling eruption and  $H_2O$ -degassing (Korenaga 2021). Because  $H<sub>2</sub>O$  weakly degasses in an atmosphere containing several tens of bars of  $CO<sub>2</sub>$  gas, this process only became efficient when a significant portion of the atmospheric  $CO<sub>2</sub>$  was sequestrated as carbonates, linking the early fate of carbon and water (Fig. 1; Gaillard et al. 2022 and references therein). This likely involved an early mode of plate tectonic overturning featuring rapidly moving proto-plates, water outgassing during shallow mantle melting, and the sequestering of carbonates into the mantle by subduction-like processes (Korenaga 2021).

Evidence for the early delivery of mantle water to Earth's surface comes from Hadean zircons (Mojzsis et al. 2001), which point to an early granitic crust and surficial waters 100 My after the Moon-forming impact. While some of this water may have also been delivered by a late veneer,

support for the presence of mantle waters comes from the high water contents in komatiites, which are ultramafic Archaean magmatic rocks formed from the deep mantle (Sobolev et al. 2019). Long thought to be dry, komatiite magmas have a high degree of molten mantle source, possibly from the mantle transition zone or an early, waterrich, mushy mantle retaining the magma ocean's water. The high water content in komatiites may also reflect water recycling by subduction-like processes that transported surface water to the source region of komatiites (Sobolev et al. 2019)—but the fast geodynamic tempo in the Hadean and the higher mantle temperatures are likely to have limited the potential for plate hydration and deep plate subduction.

By the end of the Hadean, the mantle had probably lost most of its water to form a deep surface ocean, giving rise to the metaphor of an Archean water world (Korenaga 2021). This drying out of the mantle resulted in a viscosity increase that is thought to have contributed to a slowdown in geodynamic tempo. Yet, mantle temperatures were still 200–250°C hotter than today, and numerical models point to a convection mode involving a deformable lithospheric lid and plume-like convection columns in the mantle (Gerya 2019). In this "squishy-lid" or "plumelid" tectonic mode, prolonged periods of lithospheric growth were interrupted by rapid vertical overturns involving lithospheric drips into the mantle. Interestingly, pressure–temperature paths inferred from the geological record before 3 Ga show hints for vertical overturns and larger-scale horizontal motion and proto-subduction. Numerical modeling has shown that both modes may have been active simultaneously during the late Hadean and



**FIGURE 1** Evolution of the water pipeline connecting the plane-<br>**FIGURE 1** tany interior to the atmosphere through a clockwise tary interior to the atmosphere through a clockwise geological history. (**Left**) Magma ocean ages (the first 100 million years of planet Earth) during which hydrogen partitioned between the atmosphere, molten silicate Earth, and molten metallic core. (**Right**) Solid mantle evolution from the early Archaean to the future Earth during which water is redistributed from the deepest to the shallowest reservoirs by various styles of convection. Detailed clockwise description: Accretion supplies water from two main sources: chondrites and capture of the solar nebula; escape

processes remove H from early Earth; impacts remove the early atmospheric waters; a later veneer event completed Earth's volatile inventory; formation of the first crust and presence of early oceans, as recorded by Hadean zircons; komatiite volcanism records the outgassing of an early water-rich mantle; creation of a water-world via massive outgassing; modern subduction with the production of water-rich arc magmas and the burying of water-rich lithology; the future Earth is expected to become drier at surface and wetter in its interior.

Archean (Capitanio et al. 2019). Yet, Archean "subduction" still differed significantly from the modern style of plate subduction as the crust was thicker, the lithospheric plates warmer and softer, and the mantle hotter (Chowdhury et al. 2017), likely resulting in flat subduction and frequent slab break-offs. The implications for water cycling between Earth's mantle and surface remain poorly understood. Flat subduction of crust into a hotter mantle most likely resulted in shallow devolatilization, limiting the potential for deep water recycling. Vertical lithospheric overturn events may have involved the recycling of hydrous sediments and crust as lithospheric drips sank into the mantle, but the associated fluxes are largely unconstrained. Thus, the mantle-to-surface water pipeline operated predominantly one-sided during most of the Archaean period, from the interior to the surface. This one-sided pipeline is often suggested to explain the widespread presence of surficial waters covering Archaean terrains and the rare evidence of emerged surfaces older than 2.5 Ga.

As the mantle cooled, the geodynamic mode changed into transitional tectonics, which gradually evolved towards the modern style of plate tectonics (Chowdhury et al. 2017). This transitional mode occurred at mantle temperatures about 100–150°C higher than today. It involved the stabilization of plate boundaries as lithospheric plates became stronger, continents arose, and an increase in erosion as sea level started to drop, possibly as a consequence of increased deep-water recycling by colder plates. The timing of the onset of modern-style plate tectonics, characterized by a connected plate mosaic and long-lived stable subduction zones, remains one of the biggest unresolved questions in



Water in melts

Water flux into plates and mantle Water flux into exosphere

**FIGURE 2** Cartoon of Earth's deep geological water cycles. Red arrows illustrate fluxes of water in a melt phase. During mantle melting, water partitions into the melt phase and travels with it towards submarine or subaerial eruptions centers. Magenta arrows illustrate the transfer of liquid water from the Earth's interior to the surface, referred to as the exosphere (here defined as the combination of the ocean, atmosphere, and continental crust). Dark blue arrows mark the fluxes of surface water into oceanic plates and the deeper mantle. Under the current plate tectonic regime, ingassing fluxes (dark blue) exceed mantle outgassing fluxes (magenta), resulting in a net water loss from the Earth's surface into the convecting mantle.

geodynamics (Gerya 2019). Associated is the question of how the mantle-to-surface water pipeline evolved towards its modern two-sided mode involving water outgassing and ingassing.

#### **DEEP WATER CYCLING AND MODERN PLATE TECTONICS**

For the current plate tectonic regime, water outgassing and ingassing can be simplified as in Figure 2. Outgassing can occur when the mantle melts and water partitions into the melt phase (red arrows in Fig. 2). If those melts erupt at shallow water depth or above sea level, water outgasses into the ocean/atmosphere due to its low solubility in basaltic melts at atmospheric pressure (magenta arrows, Fig. 2). Surface water, in turn, is incorporated in plates during alteration processes (dark blue arrows). During plate subduction, most of this water is returned to the Earth's surface at fore-arc vent sites and arc volcanoes (magenta arrows). At some old and cold subduction zones, water may be transported into the deeper mantle (dark blue arrows). Multiple lines of argument suggest that ingassing exceeds outgassing for the modern plate tectonic conditions (van Keken et al. 2011; Korenaga et al. 2017), which opens up the intriguing possibility that plate tectonics induces a long-term net transfer of free surface water into the mantle.

#### **WATER INCORPORATION AND THE LIFE CYCLE OF OCEANIC PLATES**

#### *Ocean Crust Formation*

New oceanic crust constantly forms along the approxi-

mately 65,000-km-long mid-ocean ridge system that encircles the Earth. The mantle source that melts to make mid-ocean ridge basalt (MORB) contains about 50–200 ppm H2O (Hirschmann and Kohlstedt 2012), which partitions into the melt phase, causing MORB to contain about 0.3 wt.% of  $H_2O$ . New seafloor is created at a rate of  $3.4 \text{ km}^2/\text{y}$  with a mean thickness of ~6 km (FIG. 3A), implying an annual magma production rate of ~20  $km<sup>3</sup>/y$ . This translates into a water flux from the mantle into the basaltic crust of 1.2 × 1011 kg /y (Hirschmann and Kohlstedt 2012). This flux does not significantly contribute to free surface water because water solubility in basaltic melts is a function of pressure, temperature, and other volatiles such as carbon dioxide. Figure 3 shows that most mid-ocean ridges are located at water depths > 2 km, where the solubility limit will not be exceeded so that the mantle water becomes structurally bound within the solidifying oceanic crust.

#### *Aging and Alterations of Ocean Plates and Intraplate Fluid Exchange*

High-temperature hydrothermal circulation manifests itself as the spectacular black

smoker systems. Fluid cycling continues off-axis at lower temperatures, where the basaltic basement is outcropping at, e.g., fracture zones, ridge flanks, and seamounts (Faccenda 2014). The extent of this alteration depends on the depth of seawater circulation and the rocks with which it interacts. At intermediate to fast-spreading ridges, where new seafloor is created at rates >50 mm/y and at a near-uniform thickness of 6 km (Fig. 3A), hydrothermal circulation extends at least down to the base of the sheeted dike complex (approximately 1.5 km depth).

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Accretion at slower spreading ridges occurs by a combination of magmatic and tectonic processes, producing crust of highly variable thickness (Fig. 3A). When the magma flux is reduced, mantle rocks become exhumed through detachment faulting, which may account for how up to 20% of slow-spread seafloor is created. In this cooler environment, tectonic faults extend up to 15 km into the ocean floor, creating pathways for seawater to react with rocks deep within the lithosphere.

Insights from ocean drilling can help to quantify the involved water fluxes (Wallmann 2001). Samples from the young oceanic crust (6–7 Ma) revealed enhanced water contents of 1.3 wt.% within the upper lavas (300–500 m), while the water content in the older Cretaceous crust (120 Ma) is higher at approximately 2.6 wt.% (Staudigel et al. 1996). The sheeted dike complex has been found to contain about 1.5 wt.% of water and gabbros less than 1 wt.%. Summation of these values and combining them with the rate of seafloor creation yields a water incorporation rate of  $1.2 \times 10^{11}$  kg/y for the upper lavas, and  $3.6-12.6 \times 10^{11}$  kg/y for the sheeted dikes and gabbros (Wallmann 2001). Most studies arrive at total values of around  $6 \times 10^{11}$  kg/y for water delivery into subduction zones by altered ocean crust (Faccenda 2014; see Supplementary Table 1 for published fluxes).

Sedimentation adds structurally bound and pore water to ocean plates. Clay minerals, originating from silicate weathering on land, are the dominant source of structurally bound water in marine sediments. Global estimates suggest that marine sediments transfer water in hydrous minerals into subduction zones at a rate of  $0.95 \times 10^{11}$ kg/y and pore water at a rate of  $8.6 \times 10^{11}$  kg/y (Plank and Langmuir 1998).

#### *Plate Bending and Upper Mantle Serpentinization*

Hydrothermal alteration of ocean plates is not restricted to the basaltic crust. Lithospheric mantle exhumed at slowspreading ridges and transform fault/fracture zone systems can react with seawater to form serpentine group hydrous minerals. An intense phase of upper mantle hydration occurs when plates bend at the trench outer rise before subducting back into the mantle. Normal faults provide the pathways for seawater to reach and react with cold mantle rocks to make serpentine (Ranero et al. 2003; Grevemeyer et al. 2018), which may dominate the water budget of subducting plates (Rüpke et al. 2004). Estimates for the average global subduction flux of water bound in the lithospheric mantle are in the range of  $3-6 \times 10^{11}$  kg/y (Supplementary Table 1). The above values suggest that ocean plates carry about  $10 \times 10^{11}$  kg/y of structurally bound water into the global subduction zones (van Keken et al. 2011; Faccenda 2014).

#### **SOURCES OF FREE WATER IN THE GEOLOGICAL WATER CYCLE**

#### *Volcanism and Mantle Water Degassing*

Magmatic processes can transfer mantle water back to the surface, and the main magmatic settings sorted by magma volumes are oceanic spreading centers, volcanic arcs, and ocean islands. At mid-ocean ridges, the hydrostatic pressure prevents the formation of a free water phase (Fig. 3B). However, when the mantle melts within rising mantle plumes at hotspots or by the fluxing of slab fluids into the mantle wedge at subduction zones, mantle water will first partition into the melt phase before exsolving and escaping into the ocean/atmosphere system during melt ascent to sub-aerial or shallow water eruption sites. These mantle water degassing fluxes, marked as red arrows in Figure 2, have been estimated to be in the range of  $0.4 \times 10^{11}$  kg/y (Wallmann 2001) to  $1.2 \times 10^{11}$  kg/y (Parai and Mukhopadhyay 2012). At this outgassing rate, it would take about 12 Gy to "make" the global ocean, which illustrates how much higher these rates must have been early in Earth's history.

#### *Water Release and Deep Recycling at Subduction Zones*

The above mantle outgassing fluxes refer to water dissolved in the mantle before decompression or flux melting. Within sub-arc melting zones, water is also added by dehydration processes driven by the increasing pressure and temperature during plate subduction. Compaction and early diagenetic reactions at shallow levels squeeze fluids from



of spreading rate. At slow spreading rates, shifting magmatic and tectonic phases form new ocean floor of variable age and composition; at fast spreading rates, basaltic ocean crust of nearly uniform thickness is produced. Most mid-ocean ridges are located at water depths of about 2–4 km.



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the subducted sediments, which are expelled at cold vent sites in the forearc region (Freundt et al. 2014). At deeper levels, when temperatures reach 400–600°C, metamorphic dehydration reactions result in fluid release from the oceanic crust and serpentinized lithospheric mantle (van Keken et al. 2011), which triggers arc melting. At the coldest subduction zones, this dehydration may be incomplete, so some water is transported into the deeper mantle (Rüpke et al. 2004; van Keken et al. 2011; Magni et al. 2014).

Freundt et al. (2014) compiled observational constraints for the water budget of the Central American subduction zone. They tried to balance water input and the various return fluxes, such as fore-arc venting, degassing at arc volcanoes, and storage in magmatic intrusions, yet could account for only about 40% of the subducted water, with the remainder potentially being recycled into the deeper mantle and/or fluxing to regions of low seismic velocities and electric resistivity identified in the upper plate. Plank et al. (2013) pointed to the surprisingly uniform average water content of approx. 4 wt.% in basaltic melt inclusions from volcanic arcs. Combining this value with estimates of magma production rates yields an arc volcanic water flux of  $1.9-3.8 \times 10^{11}$  kg/y, which is only 20%-40% of the total water input mentioned above, but similar to the predicted incomplete slab dehydration at sub-arc depth (van Keken et al. 2011).

An alternative approach is to use numerical models to resolve the thermal structure of subduction zones and to identify favorable tectonic conditions for deep water recycling. Young and hot plates tend to dehydrate completely, while rapidly subducting old plates can remain sufficiently cold to stay partially hydrated at sub-arc depths (Rüpke et al. 2004; van Keken et al. 2011; Magni et al. 2014). Global estimates based on such simulations put deep water recycling at 2–6 × 1011 kg/y (Faccenda 2014). Unfortunately, these estimates include a large uncertainty as deep water recycling critically depends on the detailed thermal structure of slabs, which remains challenging to calibrate in the employed models. As plates subduct into the hot mantle, pressure and temperature increase, triggering a sequence of metamorphic reactions that release water. While crustal and sedimentary rocks tend to dehydrate almost completely, mantle rocks may remain sufficiently cold to transport

water into the deeper mantle. This can occur when the subducting mantle evolves along a pressure–temperature path that stays on the hydrous side of the so-called "choke point" at 6 GPa and 580°C in the phase diagram of hydrous mantle rocks. If temperatures exceed 580°C at 6 GPa (approximately 185 km depth), serpentine group minerals break down and deeper water recycling is limited. If temperatures are lower, so-called dense hydrous magnesium silicates may take up the water and transport it into the deeper mantle.

With deep water recycling occurring at some of the coldest subduction zones, the question arises of how water is partitioned within the mantle. Decades of geochemical work have identified various chemical mantle end-members, with some showing clear evidence for recycled material. Current mantle processing rates are in the 5–10 Gy range, which is too slow to homogenize the mantle even on long time scales. The water content of the preserved chemical mantle

end-members differs, with the depleted MORB source showing the lowest water contents and the common FOZO

component the highest. Recycled components (HIMU, EM1, EM2) show intermediate water contents, which can be interpreted as evidence for highly efficient plate dehydration during subduction (Dixon et al. 2002). These constraints are not inconsistent with a currently ingassingdominated deep water cycle (Rüpke et al. 2006), but point to a more nuanced picture in which ingassing rates cannot be too high.

#### **EVOLUTION OF EARTH'S DEEP WATER CYCLE ON TECTONIC TIME SCALES**

The preceding paragraphs have illustrated how the age and speed of subducting plates control water input and dehydration patterns, and how the rate of seafloor creation paces the incorporation of water in oceanic plates. The interplay between these processes (and other mechanisms, such as ice sheet volume and dynamic topography) controls sea level on tectonic time scales (Conrad 2013). Figure 4 shows various published sea-level curves for the Phanerozoic over the past ~540 My. These curves suggest that sea level should not have dropped by more than 360 m due to plate subduction, with lower values appearing more realistic (Parai and Mukhopadhyay 2012; Fig. 4).

This maximum permissible sea-level drop over the Phanerozoic has been used to discriminate between successful and unsuccessful models of the geological water cycle (Rüpke et al. 2006; Parai and Mukhopadhyay 2012). Assuming other drivers of sea level change as constant, the net water ingassing fluxes over the Phanerozoic should not exceed about  $(1-3) \times 10^{11}$  kg/y to keep the associated drop in sea level within reasonable bounds of 100–300 m. Support for a long-term net water loss from Earth's surface into the deeper mantle also comes from modeling the continental freeboard, the mean elevation of the continents above sea level. Assessing continental freeboard in deep time is complex as many components of the associated isostatic balance are challenging to parameterize. In a comprehensive study, Korenaga et al. (2017) modeled that the near constancy of continental freeboard since the Early Proterozoic (~2.5 Ga) requires a long-term net water influx from the surface to the mantle of at least  $3 \times 10^{11}$  kg/y for a billion years.



**FIGURE 4** Published estimates for Phanerozoic sea level changes. The triangle outlines the maximum plausible sea level drop related to mantle net ingassing by cold plate subduction following Parai and Mukhopadhyay (2012).

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To elucidate the interrelations between water fluxes and plate tectonic parameters, Karlsen et al. (2019) compiled information on seafloor creation rate, speed and age of subducting plates, and length of subduction zones for the past 200 My. They found that sea level may have dropped by up to 130 m over the past 200 My, partly paced by major changes in spreading rate and the average age of subducting lithosphere. This more detailed link between surface water and plate tectonics was recently invoked by Boulila et al. (2023) to explain strikingly similar 36-My cycles in tectonic events, sea-level changes, diversity of marine taxa, and macrostratigraphic data over the past 250 My of Earth history.

Multiple lines of argument, therefore, suggest that Earth's deep water cycle is currently characterized by a net transfer of water into the mantle. These conditions will likely have persisted for the last 200 My (Karlsen et al. 2019), but may have extended back to 3 Ga (Korenaga et al. 2017). This takes us back to the history of hydrogen partitioning in the early Earth and the geodynamic regime during Hadean (~4.6–4 Ga) and Archean times (4–2.6 Ga). Earth has kept a remarkable balance in terms of the continental freeboard throughout most of its history, and this balance permitted the functioning of key global biogeochemical cycles, such as the weathering thermostat that ensures a temperate climate on long time scales—and we still do not fully understand these global-scale processes and feedbacks.

This review paper finishes with a series of unsolved questions. 1) Using plate tectonic reconstructions to

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constrain the geological water fluxes through time is a promising new direction, and it will be exciting to compare the higher temporal resolution of these models with archives of the evolution of seawater chemistry and sea levels. 2) Capturing the onset of water ingassing via subduction processes remains a first-order requirement for improving models of the geological history of water. 3) The duration and magnitude of early water outgassing from the mantle must be captured by deploying new proxies and improving thermomechanical models of the magma ocean solidifications. 4) It is possible that Earth's core is the most important reservoir of hydrogen, yet no consensus has been reached and it is unknown whether such hydrogen is involved in mantle convection. 5) Closer to Earth's surface, two reservoirs are particularly poorly constrained: metasomatized lithospheric roots and the water budget of intrusive magmatism.

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